

CATALYTIC DECOMPOSITION OF ACETALDEHYDE

FROM THE
THESIS

SUBMITTED TO THE GRADUATE SCHOOL OF THE
JOHNS HOPKINS UNIVERSITY IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

BY
MICHAEL S. EBERT

BALTIMORE
MAY, 1932

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CATALYTIC DECOMPOSITION OF ACETALDEHYDE¹

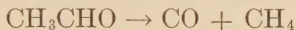
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I. INTRODUCTION

Acetaldehyde is a compound of very considerable activity. In gaseous form, under different conditions, it will undergo a number of different reactions of which the predominant one is the simple decomposition,



A study of the equilibrium that results, with the possible reversal of the reaction to synthesize acetaldehyde from carbon monoxide and methane, is of interest from both theoretical and practical standpoints.

Thermodynamical calculations for this reaction have been made. Those based on generally accepted values (e.g., Parks and Huffman (5)) of free energies for the compounds involved indicate an equilibrium very unfavorable to synthesis. There is some uncertainty involved in such calculations, but to indicate a measurable partial pressure of acetaldehyde under the experimental conditions, the error in such free energy calculations would have to be at least 15,000 cal. It is true, however, that small amounts of acetaldehyde have been produced in the electric spark (3) and by the use of silent electric discharge (4). This paper gives the results of research on catalysts for this reaction.

II. CATALYSTS

Obviously the decomposition reaction is in this case most convenient for study of the catalysts; a dynamic method was first used. In order to test a material for catalytic activity some of it was placed in glass in a furnace, and activated by a stream of hydrogen. Then several grams of acetaldehyde were passed over the activated material by use of nitrogen as the inert carrier gas. Liquid products were removed by strong cooling, and were weighed and examined; fixed gases remaining were measured and then analyzed by the usual methods of absorption and combustion. Tem-

¹ From the thesis submitted to the Graduate School of The Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1932.

² Bill Raskob Foundation Fellow, 1929-33.

perature, rate of flow of gases, volume changes, and presence of color, odor, and high-boiling fractions in the recovered liquids were also noted on each of the sixty-six runs.

Metals for the catalysts were precipitated in the form of hydroxides, either pure or with supporting materials admixed. After being washed and dried, they were reduced in a stream of hydrogen at 300°C. for copper, 400°C. for nickel, and 500°C. for iron and cobalt, and cooled in an atmosphere of purified nitrogen.

Results indicate that copper is not a catalyst for this reaction. Other investigators (2) found that copper, on the contrary, favors condensation to form paraldehyde, metaldehyde, and crotonaldehyde. Iron shows very little activity, even at 300°C. Cobalt is more active than iron, but less so than nickel, which shows marked activity even below 200°C. Cobalt catalysts produce a relatively high hydrogen content in gaseous products, and are also sensitive to a slow poisoning effect, which Russel and Marschner (6) attribute to formation of crotonaldehyde.

Supported catalysts resemble the corresponding pure metals, but siliceous supporting materials also favor extensive side reactions, producing high-boiling liquids and a very low $\text{CO}:\text{CH}_4$ ratio. Catalysts made from amalgams were less active than the corresponding reduced metal, probably because of remaining traces of mercury, exceedingly difficult to remove.

A dark green, gel-like precipitate, formed by action of excess sodium hydroxide on an 8 per cent nickel nitrate solution was, after reduction, the material showing greatest activity and most freedom from side reactions. This catalyst was used in all subsequent equilibrium studies.

III. EQUILIBRIUM STUDIES

Preliminary studies indicated that in a steel bomb the decomposition of acetaldehyde was quite slow, the reaction continuing for at least one hundred and fifty hours. It also became evident that the temperature must be limited to 175°C. or above to prevent formation of nickel carbonyl, and to 225°C. or below to prevent formation of carbon dioxide and carbon. The presence of much carbon dioxide was found to aid in preventing resin formation as well as in suppressing carbon deposition, therefore its use was adopted.

In the adopted procedure, 25 g. of acetaldehyde was sealed in one thin-walled glass tube; in a similar tube 15 g. of catalytic material was reduced with hydrogen at 400°C. for three hours and sealed. Both sealed tubes were placed in the 485-cc. steel bomb, the bomb then closed, evacuated, filled with carbon dioxide to a pressure of 735 lbs. per square inch, and finally the glass tubes were smashed. Small samples of the contents were blown off at about twelve-hour intervals for analysis by a method similar to that of Ripper (1). This method involved collection of the sample over

mercury, absorption in strong sodium bisulfite solution, and determination of acetaldehyde by the use of strong iodine solution and dry sodium bicarbonate, and titration with standard iodine solution. The method is reported to be satisfactorily specific for acetaldehyde in the presence of only small amounts of higher aldehydes, and involves a possible experimental error in absorption and titration estimated to be equivalent to 0.03 "per cent by volume." Residual gases were analyzed by absorption and combustion for carbon dioxide, carbon monoxide, methane, ethane, hydrogen and unsaturated hydrocarbons.

Table 1 contains the results of one run made according to the above procedure. The temperature was first held at 200°C., then lowered and held at 175°C. The increase in aldehyde content following the lowering of

TABLE 1
Change of aldehyde in bomb

TEMPERATURE	ELAPSED TIME	ALDEHYDE
<i>degrees C.</i>	<i>hours</i>	<i>per cent by volume</i>
200 $\pm$ 2	12	1.85
	35	1.74
	60	1.01
	108	0.38
	117	0.36
	141	0.28
	167	0.25
175 $\pm$ 2	179	0.25
	204	0.28
	494	0.34
	515	0.31

the temperature seems to indicate attainment of equilibrium, although the actual amounts present are quite small. A corresponding slight decrease of both carbon monoxide and methane content also occurred. On opening the bomb a very slight amount of free carbon and several cubic centimeters of liquid but no resinous material was found.

Previously in the course of catalyst studies, an approximately equimolar mixture of carbon monoxide and methane was passed over an active catalyst at 175°C. and atmospheric pressure and through a liquid air trap. After the liquefied methane had boiled away, a definite odor of acetaldehyde was observed, and the rinsings of the bulb gave a weak positive test to fuchsine reagent. The results, however, could not be repeated.

Three attempts at synthesis were made by sealing in a glass tube of about 15-cc. volume, approximately 5.0 g of activated catalyst, 0.01 mole of liquid methane, and 0.02 mole of carbon monoxide in the form of nickel

carbonyl, then heating the tube under high external pressure in a bomb at 170–190°C. for about sixty hours. Neither acetaldehyde nor any resin which would be evidence of temporary existence of acetaldehyde could be detected.

IV. SUMMARY

Numerous catalysts for the decomposition of acetaldehyde into carbon monoxide and methane have been studied; nickel precipitated by sodium hydroxide and reduced with hydrogen at 400°C. proved to be the best. Equilibrium conditions have apparently been attained in one direction, but attempts to approach them in the direction of synthesis were not very successful.

REFERENCES

- (1) See CLAUSEN: J. Biol. Chem. **52**, 263 (1922).
- (2) KOMATSU AND KURATO: Mem. Coll. Sci. Kyoto Imp. Univ. **7A**, 293 (1924).
- (3) LOSANITSCH: Ber. **44**, 315 (1911).
- (4) LOSANITSCH AND JOVITSCHITSCH: Ber. **30**, 137 (1897).
- (5) PARKS AND HUFFMAN: Free Energies of Some Organic Substances, A. C. S. Monograph No. 60. The Chemical Catalog Co., Inc., New York (1932).
- (6) RUSSEL AND MARSCHNER: J. Phys. Chem. **34**, 2554 (1930).

BIOGRAPHY

Michael S. Ebert was born in York, Pennsylvania, on the sixteenth of February, 1907. Two years later his parents moved to Wilmington, Delaware. He attended the primary schools of this city and the Wilmington High School during the four years 1921 to 1925. In the autumn of 1925 he was admitted to the Department of Chemistry of Lehigh University, from which institution he was graduated in June, 1929, with the degree of Chemical Engineer. He entered the Department of Chemistry of the Faculty of Philosophy of the Johns Hopkins University in the autumn of the same year, and since that time he has been connected with that department as a candidate for the degree of Doctor of Philosophy.



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